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THE DETECTION OF SMALL QUANTITIES OF METHYL ALCOHOL IN THE PRESENCE OF ETHYL ALCOHOL.*

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THE greater number of the many methods proposed for the detection of small quantities of methyl alcohol in the presence of ethyl alcohol depend on the oxidation of the mixed alcohols to their respective aldehydes, and then subsequently testing for formaldehyde, ethyl alcohol being supposed to form only acetaldehyde. A heated copper spiral, potassium permanganate, and potassium dichromate, have been employed as oxidising agents.—Prescott (*Pharmaceutical Archives*, 1901, **4**, 86); Trillat (*ANALYST*, 1899, **24**, 13); Sanglé-Ferrière and Cuniasse (*ibid.*, 1903, **28**, 148).

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I find that traces of formaldehyde are invariably produced by the oxidation of pure ethyl alcohol; hence it is almost impossible to detect small quantities of methyl alcohol in ethyl alcohol by any oxidation method. When, however, more than 5 per cent. of methyl alcohol is present, a definite result may be obtained.

I have tried the various tests which have been recommended for the recognition of formaldehyde in the mixture of the aldehydes, but none were found to be as delicate as the following one: Formaldehyde and morphine in the presence of strong sulphuric acid yield an intense violet colour, whereas acetaldehyde under similar conditions gives an orange colour. The test is best performed by adding a few drops of $\frac{1}{2}$ per cent. solution of morphine hydrochloride to the dilute solution of formaldehyde contained in a test-tube, and then carefully pouring some strong sulphuric acid down the side of the tube, so as to form a layer beneath the formaldehyde. A deep violet blue ring is obtained at the junction of the liquids. This test is exceedingly delicate, and capable of detecting as little as one part of formaldehyde per million. The deep orange colour produced by acetaldehyde would mask a trace of formaldehyde; formaldehyde and acetaldehyde may, however, be readily separated from one another by distillation. When an aqueous solution of acetaldehyde and formaldehyde is gently distilled, the whole of the acetaldehyde distils over first, and the formaldehyde after.

On oxidising pure ethyl alcohol, and separating by distillation all the acetaldehyde produced, traces of formaldehyde were always present, which gave a faint violet ring with the morphine test. The addition of about 5 per cent. methyl alcohol to the ethyl alcohol gave a very decided colour reaction, which could not be mistaken for the reaction yielded by the pure ethyl alcohol. The amount of formaldehyde formed from ethyl alcohol varied considerably with the conditions of the oxidation; the more vigorous the reaction, the greater the formation of formaldehyde. Thus, with the heated copper spiral or with excess of alkaline permanganate the amount of formaldehyde formed is marked, but with ammonium persulphate the amount is comparatively small. With dichromate and sulphuric acid, if the mixture be strong, so that oxidation takes place on the application of slight or no external heat, then a considerable amount of formaldehyde is produced, whereas if the oxidising mixture be very dilute and not in excess, the amount produced is exceedingly small. As a result of numerous experiments I find that the following is the most satisfactory method for the detection of methyl alcohol in ethyl alcohol, remembering that a quantity corresponding with less than 5 per cent. of the ethyl alcohol present cannot be detected with certainty: 1 cubic centimetre of the mixed alcohols is placed in a small, round-bottomed distilling-flask, then the oxidising agent is added. If ammonium persulphate is used, 0.8 gram of the salt is added, followed by 3 c.c. of dilute sulphuric acid (1 in 5); or in the case of potassium dichromate, 1.5 grams of the salt and 1.5 grams of pure sulphuric acid. In both cases the mixture is diluted with water to 20 c.c.; the flask is then connected to a small condenser, and heated quickly over the naked flame of a Bunsen burner, the distillate being collected in test-tubes in five separate portions of 2 c.c. at a time. The first two portions, which will contain all the acetaldehyde, may be rejected. To each of the remaining portions a few drops of $\frac{1}{2}$ per cent. solution of morphine hydrochloride are added.

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and strong sulphuric acid is poured into each test-tube so as to form a layer at the bottom. In the presence of formaldehyde a violet ring will be formed at the junction of the liquids.

In conclusion, I desire to express my indebtedness to Mr. A. C. Chapman, for advice given to me in connection with this work.

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